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Tuning the link of doubly silyl-bridged ferrocenes

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Abstract

New 4,4,8,8-tetraalkyltetrahydro-4,8-disila-*s*-indacene ligands were synthesized in order to increase the solubility of higher-nuclear bridged metallocenes. CpNa and R_2SiCl_2 (R = Et, *n*-Bu) gave the silylated cyclopentadienes $(C_5H_5)SiR_2Cl$ that were converted to disila-*s*-indacenes carrying R at the silyl bridges. Deprotonation led to the corresponding dianions, which after addition of CpNa, reacted with solvated iron dichloride to yield dinuclear ferrocenes that were bridged by R_2Si groups. In any case, mixtures of *syn*- and *anti*-isomers were obtained from which the pure *anti*-isomers could be separated by crystallization. All compounds were characterized by ^1H- and ^{13}C-NMR spectroscopies and partly by mass spectroscopy. In cyclic voltammetry, the *anti*-isomers of the dinuclear ferrocenes underwent successive electron transfers with separations that were determined by solvation effects. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocenes; Silyl bridges; Bimetallic compounds; Cyclic voltammetry

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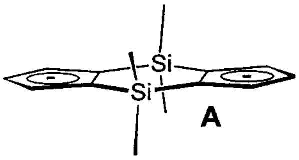
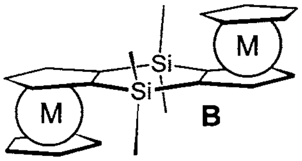
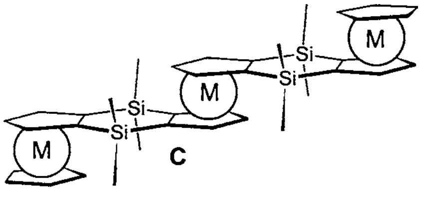
1. Introduction

Soon after introducing the doubly silyl-bridged dicyclopentadienyl dianion $TMDSI^{2-}$ **A** (TMDSI stands for 4,4,8,8-tetramethyltetrahydro-4,8-disila-*s*-indacene) as a ligand [1], it proved to be very useful for linking various transition metal Cp fragments [2]. One of the advantages of **A** is the straightforward formation from the isomeric cyclopentadiene precursors in a step-by-step deprotonation that allows the synthesis of both the homo- [2,3] and heterobimetallic [3,4] compounds, among them the linked metallocenes of type **B** and **C**. It has been conjectured that such species might be useful catalysts [2c] but this has still to be demonstrated. Another attractive topic is the interaction between the organometallic building blocks, e.g. in compounds **B** and **C**, in such a way that new properties emerge that are not simply the sum of individual properties of each building block. Examples are the manipulation of the redox potentials of the di- and trinuclear metallocenes and their ligand-promoted magnetic interactions [3,4].







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Once the synthesis of di- and trinuclear model compounds has been achieved and their properties known, it is desirable to extend this chemistry to higher-nuclear or even polymeric products. When working with ligand **A** it turned out that the solubility in common solvents decreases rapidly with increasing nuclearity. For instance, the low solubility of tetranuclear ferrocenes strongly hampered NMR spectroscopic studies [5], and higher-nuclear analogs are expected to be virtually insoluble. An exception is the cyclic heptamer [6] that owes its still moderate solubility to the Cp ligands and the methyl groups, which constitute a kind of hydrocarbon coating at the surface of the cycle.

Synthesizing cyclic oligomers that contain the (bent) ligand **A** does not seem to be a general method for increasing the solubility, because it did not work for the corresponding cobaltocenes and nickelocenes [6]. Rather, substitution of the five-membered rings of **A** and modifying the bridges between them appeared promising. The bridges of **A** or its precursors have been modified previously [7], although tuning the solubility of the metal complexes derived thereof has not been the primary goal of that work. In most cases, one of the $SiMe_2$ bridges was substituted for CMe_2, SiMePh, $GeMe_2$ and $SnMe_2$ bridges. For the present work, it seemed more advantageous to introduce hydrocarbon chains at the silicon bridges of **A**. Also, the bridges should be identical, because this would reduce the number of isomers of bridged metallocenes that contain more than two metallocenes. This paper reports on the ethyl- and *n*-butyl-substituted ligands TEDSI–H_2 and TBDSI–H_2 (acronyms analogous to TMDSI, see above), respectively, their dianions and their dinuclear iron derivatives.

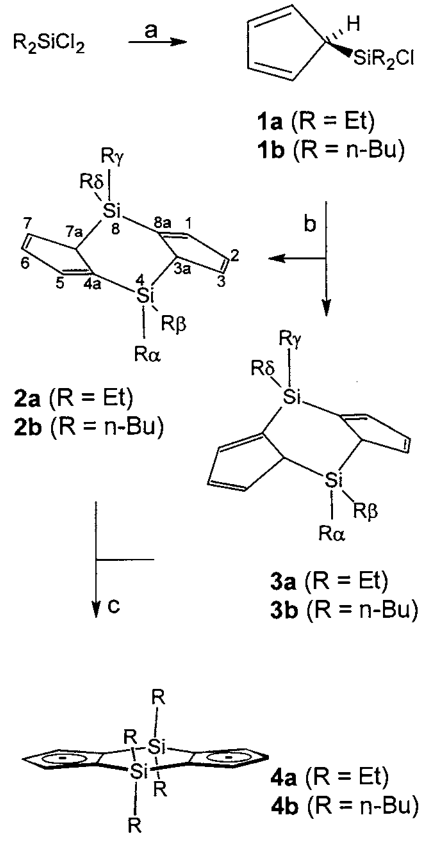
2. Results and discussion

2.1. Syntheses

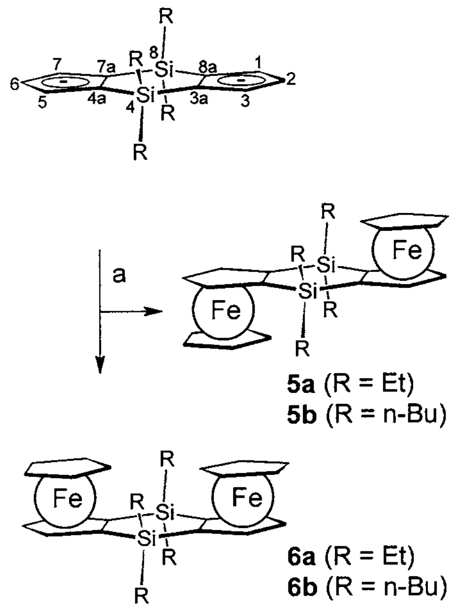
The synthesis of the new silyl-bridged Cp ligands started from Et_2SiCl_2 or *n*-Bu_2SiCl_2. *n*-Bu_2SiCl_2 was obtained in 74% yield by reacting Ph_2SiCl_2 with *n*-BuLi, and by proto-dearylating the resulting $Ph_2Si(n\text{-}Bu)_2$ with HCl. The reaction sequence from the silanes R_2SiCl_2 to the ligands is shown in Scheme 1.

The intermediate substituted cyclopentadienes **1a**/**1b** were mentioned in the literature [8] but only poorly characterized. They proved rather unstable, and reasonable yields were only obtained after rapid work-up, including distillation. Formal HCl elimination from $CpSiR_2Cl$ produced the ethyl-substituted isomers **2a**/**3a** and the *n*-butyl-substituted isomers **2b**/**3b**. The equilibrium isomer ratios at 298 K were 2/1 for **2a**/**3a** and 4/1 for **2b**/**3b** as determined by the integration of corresponding ^1H- and ^{13}C-NMR signals. It follows that the C_i-symmetric isomers **2a**/**2b** are less affected by big alkyl groups at the silicon than the C_s-symmetric isomers **3a**/**3b**. For the ethyl derivatives **2a**/**3a**, different purification procedures were tested. It turned out that the yield was higher after medium pressure liquid chromatography (MPLC) than after distillation. **2a**/**3a** and **2b**/**3b** were obtained as liquids of low and high viscosity, respectively. By contrast, the methyl derivative has been shown to crystallize from solution [9] or after sublimation [1b]. Double deprotonation of **2a**/**3a** and **2b**/**3b**, which may be conducted step by step (Scheme 2), gave the dianions **4a** and **4b** in up to quantitative yield. Starting from the dialkyldichlorosilanes, yields of 55% for **4a** and 26% for **4b** were obtained.

The subsequent reaction to the dinuclear ferrocenes is summarized in Scheme 2. Besides **5a**/**6a** and **5b**/**6b**, Cp_2Fe and higher-nuclear ferrocenes were formed. An excess of CpNa was used in order to keep the yield of oligomers low. As a consequence, more Cp_2Fe was produced. However, Cp_2Fe can easily be removed by sublimation and MPLC. After prolonged sublimation, first a small band of Cp_2Fe developed in MPLC, which was followed by much larger bands that con-



Scheme 1. Synthesis of the silyl-bridged Cp anions TEDSI^{2-} (**4a**) and TBDSI^{2-} (**4b**). (a) CpNa; (b) one equivalent of *n*-BuLi; (c) two equivalents of *n*-BuLi.



Scheme 2. Synthesis of the dinuclear ferrocenes; (a) excess CpNa, $FeCl_2(THF)_n$.

tained **5a**/**6a** and **5b**/**6b**, respectively. The *anti*-isomers **5a** and **5b** were NMR spectroscopically pure after fractional crystallization, while samples of the *syn*-isomer **6a** always contained small amounts of the *anti*-isomer. Thisis in contrast to the methylated *syn*- and *anti*-isomers that could be separated straightforwardly [5].

As anticipated, the ethyl- and *n*-butyl-substituted dinuclear ferrocenes were much more soluble in hydrocarbons and polar solvents than were the methyl-substituted analogs. Probably, this also rendered the isomer separation more difficult. All higher-nuclear ferrocenes that were left behind after separating the dinuclear species **5** and **6** could be dissolved in THF, thus greatly facilitating future studies of these species.

2.2. Redox behavior

The cyclic voltammograms of **5a** and **5b** showed two waves corresponding to the successive electron transfers (ETs) that yield the mono- and dications (see Table 1 for data). According to the ΔE_p values (ΔE_p = separation of the anodic and cathodic peak potentials), the ETs are almost reversible, as usually found for substituted ferrocenes. It is also common that the first oxidation potential $E_{1/2}(1)$ is lower than that of Cp_2Fe owing to electron delocalization within the monocation. As for the separation of successive ETs ($\Delta E_{1/2}$) there is a distinct decrease of $\Delta E_{1/2}$ when the substituents at silicon are changed from R = Me to R = Et and *n*-Bu. Because the compounds are very similar geometrically and electronically, the observed trend can hardly be ascribed to different coulombic interactions, substituent effects and electron delocalization. Rather, it should be due to solvation effects. Thus, when the chain length of R increases, the solvation of the neutral species, the monocation and the dication becomes increasingly similar. In the same order, the contribution of differential solvation to $\Delta E_{1/2}$ decreases as found experimentally.

2.3. ^1H-, ^{13}C- and ^{29}Si-NMR characterization

The new silyl-bridged cyclopentadienes **2a**, **2b**, **3a** and **3b** are fluxional molecules that undergo 1,2-silatropic shifts similar to the Me_2Si-bridged derivatives [1b,3]. Here the authors restrict themselves to the low-temperature limiting spectra, whose details are listed in Table 2. For **2a**/**3a**, the NMR data were obtained by using two-dimensional techniques, such as ^1H, ^1H DQF COSY and ^1H, ^{13}C HMQC [10]. The data of **2b**/**3b** result from using standard ^1H- and ^{13}C-NMR experiments and comparison with **2a**/**3a**, while the ^{29}Si-NMR spectra were recorded by using DEPT.

The ^1H- and ^{13}C-NMR signals of the dianions **4a** and **4b** and of the dinuclear ferrocenes **5a**, **5b** and **6a** were identified by one-dimensional spectra, which may be decomposed into two parts (see Table 3). One set belongs to the η^5-bound Cp fragments whose signal assignment follows from the ^1H- and ^{13}C-NMR integrals. The other set represents the alkyl groups bound to Si. The ethyl groups of **5a** give rise to an ABC_3 spin system in the ^1H-NMR spectrum. The corresponding pattern can be simulated with $\delta_A = 1.29$ ppm, $\delta_B = 1.19$ ppm, $\delta_C = 1.39$ ppm, $^2J_{H-C-H} = 13.2$ Hz and $^3J_{H-C-C-H} = 7.4$ Hz. In contrast, **6a** has two sets of ethyl groups each of which shows the common A_2B_3 pattern. In the ^{13}C-NMR spectrum, the CH_2 and CH_3 signals of **5a** and **6a** were distinguished by using 135° DEPT.

Table 1
Electrochemical results[a] of the dinuclear ferrocenes bridged by R_2Si groups

	R = Me[b]	R = Et (**5a**)	R = *n*-Bu (**5b**)
$E_{1/2}(1)$	−45	−20	−10
$\Delta E_p(1)$	80	75	65
$E_{1/2}(2)$	165	185	185
$\Delta E_p(2)$	80	70	70
$\Delta E_{1/2}(2–1)$	210	205	195

[a] All values are given in mV, the potentials $E_{1/2}$ are relative to that of Cp_2Fe/Cp_2Fe^+, temperature 25°C, scan rate 200 mV s^{-1}, solvent propionitrile, supporting electrolyte 0.10 molar n-Bu_4NPF_6. Successive oxidations are numbered in parentheses.

[b] Data taken from [5].

Table 2
^{1}H-, ^{13}C- and ^{29}Si-NMR results[a] of the silyl-bridged cyclopentadienes

Nucleus and position[b]	Compound			
	2a	**2b**	**3a**	**3b**
H-1	7.09	6.87[c]	6.99	6.87[c]
H-2	6.82	6.87[c]	6.62	6.87[c]
H-3	6.89	6.87[c]	6.86	6.87[c]
H-3a	3.58	3.54	3.92	3.85
H-4a			3.92	3.85
H-5	7.09	6.87[c]	6.86	6.87[c]
H-6	6.82	6.87[c]	6.62	6.87[c]
H-7	6.89	6.87[c]	6.99	6.87[c]
H-7a	3.58	6.87[c]		
α-Si–CH_2	1.14	1.96–0.99	−0.47	1.96−0.99
β-Si–CH_2	0.26	1.96–0.99	1.14	1.96–0.99
γ-Si–CH_2	1.14	1.96–0.99	0.93	1.96–0.99
δ-Si–CH_2	0.26	1.96–0.99	0.93	1.96–0.99
α-CH_3	0.85	1.96–0.99	0.62	1.96–0.99
β-CH_3	1.32	1.96–0.99	1.32	1.96–0.99
γ-CH_3	0.85	1.96–0.99	1.14	1.96–0.99
δ-CH_3	1.32	1.96–0.99	1.14	1.96–0.99
C-1	140.9	140.8	140.0	139.9
C-2	131.2	131.5	131.5	131.5
C-3	138.7	138.8	137.1	137.2
C-3a	56.4	56.7	56.4	55.0
C-4a	143.6	144.2	56.4	55.0
C-5	140.9	140.8	137.1	137.2
C-6	131.2	131.2	131.5	131.5
C-7	138.7	138.8	140.0	139.9
C-7a	56.4	56.7	145.6	146.2
C-8a	143.6	144.2	145.6	146.2
α-Si–$C\mathrm{H}_2$	−0.7	[d]	5.1	[d]
β-Si–$C\mathrm{H}_2$	4.7	[d]	8.5	[d]
γ-Si–$C\mathrm{H}_2$	−0.7	[d]	8.1	[d]
δ-Si–$C\mathrm{H}_2$	4.7	[d]	7.3	[d]
α-$C\mathrm{H}_3$	7.9	[d]	8.5	[d]
β-$C\mathrm{H}_3$	8.2	[d]	8.2	[d]
γ-$C\mathrm{H}_3$	7.9	[d]	8.2	[d]
δ-$C\mathrm{H}_3$	8.2	[d]	8.2	[d]
Si-4	−3.06		8.99	
Si-8	−3.06		−14.92	

[a] δ values at r.t. relative to TMS. Solvent C_6D_6.

[b] For numbering see Scheme 1.

[c] Multiplet.

[d] Partly unresolved resonances of n-Bu: 3.54, 14.0, 14.4, 26.7 and 27.0 ppm.

3. Experimental

The syntheses and spectroscopic investigations were carried out under purified nitrogen in dry and oxygen-free solvents. Equipment purchased from Kronlab was used for medium pressure liquid chromatography (MPLC) as described previously [3]. Also see Fritz et al. [3] for cyclic voltammetry equipment. The elemental analyses were obtained from the microanalytical labo-ratory of this Institute. The NMR spectra were recorded on a JEOL Lambda 400 and a Bruker MSL 300 instrument, the mass spectra on a Varian MAT 311 A instrument.

*3.1. Tetrahydro-4,4,8,8-tetraethyl-4,8-disila-s-indacene (**2a**/**3a**)*

Dry CpNa · 0.4THF (9.2 g, 104 mmol) was suspended in diethyl ether and cooled to −78°C. A cooled mixture (−78°C) of 16 ml (104 mmol) diethyldichlorosilane in diethyl ether was added quickly under vigorous stirring. While being stirred for 12 h, the mixture was allowed to warm to ambient temperature, whereupon a solid separated from a cloudy solution. The liquid was filtered over $NaSO_4$, and after removal of the solvent, the remainder was distilled (40°C, 25 cm Vigreux column, 10^{-4} bar) to give 14.8 g (79 mmol, 76% yield) of cyclopentadienyldiethylchlorosilane **1a**.

1a (main isomer): ^{1}H-NMR (400.18 MHz, 293 K, $CDCl_3$): δ 6.69 (br, vinyl-H), 6.54 (br, vinyl-H), 3.66 (br, allyl-H), 0.98 (t, $^3J_{H-H} = 7.7$ Hz), 0.65 (q, $^3J_{H-H} = 7.7$ Hz). ^{13}C-NMR (100.64 MHz, 293 K, $CDCl_3$): δ 132.36 (vinyl-C), 131.70 (vinyl-C), 51.22 (allyl-C), 7.0 (CH_3), 6.9 (CH_2).

After distillation, **1a** was immediately dissolved in pentane, cooled to −78°C, and mixed with 79 mmol of n-BuLi in hexane. After 12 h the suspension was filtered, the solvent was removed, and the resulting brown oil was purified by kugelrohr distillation (MPLC was also successful) to yield 8.7 g (73% relative to **1a**) of a mixture of **2a** and **3a** as a yellow oil.

*3.2. Tetrahydro-4,4,8,8-tetra-n-butyl-4,8-disila-s-indacene (**2b**/**3b**)*

In a procedure similar to that described for **2a**/**3a**, 26.5 g (300 mmol) of CpNa · 0.4THF was allowed to react with one equivalent (65.1 g, 300 mmol) of di-n-butyldichlorosilane. The product was distilled (95°C, 10 cm Vigreux column, 10^{-4} bar) to yield 44.8 g (62%) of **1b** as a yellow oil.

1b (main isomer): ^{1}H-NMR (270.17 MHz, 293 K, $CDCl_3$): δ 6.69, 6.54, 3.66, 0.98 (t, $^3J_{H-H} = 7.7$ Hz), 0.65 (q, $^3J_{H-H} = 7.7$ Hz). ^{13}C-NMR (67.94 MHz, 293 K, $CDCl_3$): δ 132.36 (vinyl-C), 131.70 (vinyl-C), 51.22 (allyl-C), 7.0 (CH_3), 6.9 (CH_2).

Further reaction of 42.8 g (176 mmol) of **1b** in 600 ml of pentane with one equivalent (70.5 ml, 2.5 molar in hexane) n-BuLi to a mixture of **2b** and **3b**, which was purified by column chromatography over silica (60–230 mesh). The yield was 31.2 g (43%).

*3.3. Tetrahydro-4,4,8,8-tetraethyl-4,8-disila-s-indacene-3a,7a-diyldilithium (**4a**)*

Reaction of **2a**/**3a** (8.7 g, 29 mmol) with two equivalents of n-BuLi (34 ml, 1.7 molar solution) in hexane at −78°C yielded 7.6 g (83%) of **4a** as a white precipitate, which was filtered and dried under reduced pressure.

Table 3
^{1}H-, ^{13}C- and ^{29}Si-NMR results[a] of the silyl-bridged Cp anions and ferrocenes

Nucleus and position	Compound				
	4a	**4b**	**5a**	**5b**	**6a**
H-1,3,5,7	5.78	6.05	4.34	4.20	4.25
H-2,6	5.59	8.85	4.41	4.32	4.41
C_5H_5			3.95	4.07	4.24
Si–CH_2	0.97	[c]	1.06	[d]	1.20, 0.78
CH_3	0.97	[c]	1.19	[d]	1.37, 0.70
C-3a,4a,7a,8a	117.7	120.3	77.8	74.0	76.3
C-1,3,5,7	112.6	114.7	76.7	73.8	75.8
C-2,6	107.5	110.3	73.9	68.9	74,8
C_5H_5			69.6	68.5	69.4
Si–CH_2	10.7	[e]	8.9	[f]	10.3, 9.9
CH_3	9.4	16.1	9.4	14.1	9.1, 8.8
Si-4,8			−3.81	−5.78	−3.52

[a] δ values at r.t. relative to TMS. Solvent DMSO-d_6 for **4a**, HMPA-d_{18} for **4b**, and C_6D_6 for **5a**/**b**, **6a**/**b**.
[b] For numbering see Scheme 2.
[c] ^{1}H-NMR resonances of *n*-Bu: 1.40, 1.19, 0.78 and 0.61 ppm.
[d] ^{1}H-NMR resonances of *n*-Bu: 1.44, 1.14, 0.95 and 0.74 ppm.
[e] ^{13}C-NMR resonances of *n*-Bu–CH_2: 29.9, 29.5 and 21.7 ppm.
[f] ^{13}C-NMR resonances of *n*-Bu–CH_2: 27.3, 26.9 and 14.0 ppm.

3.4. *Tetrahydro-4,4,8,8-tetra-n-butyl-4,8-disila-s-indacene-3a,7a-diyldilithium* ***(4b)***

As described for **4a**, 0.53 g (1.29 mmol) of **2b**/**3b** reacted with two equivalents of *n*-BuLi (1.52 ml, 1.7 molar solution) to give 0.52 g (1.22 mmol, 95% yield) of **4b**.

3.5. *Bis[(cyclopentadienyl)iron]-μ-(1,2,3,3a,8a-η^5:4a,5,6,7,7a-η^5-3a,4,7a,8-tetrahydro-4,4,8,8-tetraethyl-4,8-disila-s-indacene-3a,7a-diyl)* ***(5a/6a)***

When a tenfold excess of solid CpNa · 0.4THF (4.5 g, 39 mmol) was added at ambient temperature to a suspension of 1.0 g (32 mmol) of **4a** in 150 ml of THF, a clear solution was obtained after stirring for a few minutes. Addition of 5.5 g (23 mmol) of $FeCl_2 \cdot 1.5THF$ led to an orange solution. After stripping the solvent, ferrocene was removed from the solid by sublimation (10^{-4} bar, 50°C). The remainder was dissolved in a minimum amount of hexane and subjected to MPLC, which yielded a narrow band (ferrocene) followed by a broad band. After elution of the latter, removal of the solvent under reduced pressure gave 0.9 g (53% relative to **4a**) of a mixture of orange **5a** and **6a** as a microcrystalline solid. After fractional crystallization from hexane at −20°C, 20 mg of pure (^{1}H-NMR) **5a** was obtained.

Found: C, 62.25; H, 6.77. $C_{28}H_{36}Fe_2Si_2$ (540.2) requires C, 62.23; H, 6.71; Fe, 20.67; Si, 10.39. CI–MS *m*/*z* (%) 539.2 (100) [M^+-H], 510.1 (67) [M^+-H–Et].

3.6. *Bis[(cyclopentadienyl)iron]-μ-(1,2,3,3a,8a-η^5:4a,5,6,7,7a-η^5-3a,4,7a,8-tetrahydro-4,4,8,8-tetra-n-butyl-4,8-disila-s-indacene-3a,7a-diyl)* ***(5b/6b)***

A sample of 3.14 g (7.4 mmol) of **4b** and 3.8 g (33 mmol) of CpNa · 0.4THF was dissolved in 200 ml of THF and mixed with 6.77 g (28.8 mmol) of $FeCl_2 \cdot 1.5THF$. After work-up as described for **5a**/**6a**, a mixture of **5b** and **6b** was obtained. Recrystallization from benzene gave 1.68 g (35% relative to **4b**) of pure (^{1}H-NMR) **5b**.

M.p. 118°C. CI–MS *m*/*z* (%) 652 (100) [M^+], 595 (8.0) [M^+-C_4H_9], 532 (14.7) [M^+-Cp–C_4H_9], 475 (1.7), 532, C_4H_9]. Found: C, 65.97; H, 7.91; Fe, 17.25; Si, 8.91. $C_{36}H_{52}Fe_2Si_2$ (652.7) requires C, 66.25; H, 8.03; Fe, 17.11; Si, 8.60.

Acknowledgements

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